

Reactions of Fatty Materials With Oxygen. XV.¹ Formation of 9,10-Dihydroxystearic Acid and Cleavage Products in the Oxidation of Oleic Acid and Methyl Oleate in Acetic Acid²

825

H. B. KNIGHT, E. F. JORDAN JR., R. E. KOOS, and DANIEL SWERN, Eastern Regional Research Laboratory,³ Philadelphia, Pennsylvania

THE prolonged autoxidation of unsaturated fatty materials in the absence of solvents leads eventually to highly viscous products through which efficient dispersion of oxygen is extremely difficult (11). The obvious solution, namely, use of a diluent, is complicated by the problem of finding an "inert" material. Consideration of possible "inert" solvents, as well as examination of the literature, indicated that glacial acetic acid most nearly meets the requirements and, in addition, it possesses the characteristic of accelerating autoxidation reactions (1, 5, 13).

This paper describes the results obtained in the autoxidation of oleic acid and methyl oleate at 25-30°, 65°, and 115-120°C. in acetic acid solution with cobalt acetate (or occasionally cobalt oleate) as the catalyst. Samples were withdrawn at suitable time intervals, the acetic acid was recovered, and the non-volatile residue was worked up to isolate 9,10-dihydroxystearic acid, short-chain cleavage products (mono- and dibasic), unoxidized and monohydroxy materials, and polymers.

Experimental

Materials Used. The oleic acid and methyl oleate (composition: oleic, 94-98%; linoleic, 0.3%; saturates, 2-6%) were prepared from olive oil (7). Cobaltous acetate and glacial acetic acid were analytical reagent grade. Cobaltous oleate was prepared from purified oleic acid as described previously (11).

Autoxidation Procedure. A typical experiment at 65° is described in detail. (Tables I, II, and III summarize the results obtained at 25-30°, 65°, and 115-120°). A solution consisting of 1,000 g. of oleic acid (or methyl oleate), 10.1 g. of cobaltous acetate (or 33 g. of cobaltous oleate), and 2,000 ml. of glacial acetic acid was prepared in a 5-l., three-neck flask equipped with a thermometer, a reflux condenser, and two fritted discs immersed in the solution. A vigorous stream of air or cylinder oxygen was passed through the solution while the temperature was maintained at 65°. Samples of the solution (ca. 450-500 ml.) were withdrawn at suitable time intervals for isolation and analysis of oxidation products.

The acetic acid was recovered under reduced pressure and the residue analyzed. The oxidation was stopped when the iodine number became substantially constant (5-10); this usually required 150-250 hours at 65°. The peroxide values were negligible throughout.

The residue was refluxed for six hours with an excess of 6 *N* aqueous sodium hydroxide, acidified while hot with 6 *N* sulfuric acid, and stirred vigor-

ously. A dark brown viscous oil separated. After the mixture had cooled to room temperature, it was treated with ether and the aqueous layer was reextracted. The combined ether solutions, in which a considerable quantity of insoluble white solid was suspended, was washed three times with small quantities of water to remove excess sulfuric acid and salt. These washings were reextracted with ether, and all ether solutions were then combined. The ether:solute ratio was approximately 3:1 at this point. The ether solution was cooled to 0 to 5° and filtered, and the solid was washed once with a small amount of cold ether. The precipitate was substantially pure high-melting 9,10-dihydroxystearic acid, m.p. 129-130° and neutralization equivalent, 317-323. A mixed melting point with an authentic sample, m.p. 130-131°, showed no depression. The yield was 12-17%, depending on the oxidation time (Table II). [An additional 1-2% of slightly impure high melting 9,10-dihydroxystearic acid, m.p. 120-123°, could be obtained by evaporation of the ether, solution of the residue in acetone (5 ml. per g. of solute) and cooling to -20°, followed by recrystallization of the precipitate from 95% ethanol at 0°.]

The dark-brown viscous residue obtained after recovery of the ether was converted to methyl esters by refluxing for eight hours with a large excess of anhydrous methanol (sulfuric acid catalyst). These esters were distilled from a Claisen flask to a maximum pot temperature of 230°/0.1 mm. Two overhead fractions, b.p. 60°/4-160°/0.4 mm. and 140°/0.05-200°/0.1 mm. were taken. Results are summarized in Table II. Maximum yields of cleavage products were 64-68%; polymer yields were 11-22%.

Discussion

Tables I, II, and III summarize the results obtained in the oxidation of oleic acid at 25-30° (room temperature), 65°, and 115-120° (the reflux temperature of the reaction mixture), respectively.

At an oxidation temperature of 65° the yield of high-melting 9,10-dihydroxystearic acid remains fairly constant between 12-17% (Table II). At 25° (Table I) and 115-120° (Table III) the yield is lower during the oxidation periods studied. At 115-120° the yield increases from 2% after 4 hours of oxidation to 11% after 128 hours; at 25-30° the yield appears to reach a maximum of 16% after 500 hours and then drops.

The best yields (64-68%) of cleavage products are also obtained at 65° (Table II). Examination of the iodine and saponification numbers of the cleavage products obtained after 256 hours of oxidation indicates that unoxidized material probably does not exceed 10% of this fraction. On the other hand, at room temperature (Table I) or the boiling point (Table III) the yields of cleavage products are consid-

¹Paper XIV is reference 10.

²Presented at the Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., Nov. 2-4, 1953.

³One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Service, U. S. Department of Agriculture.

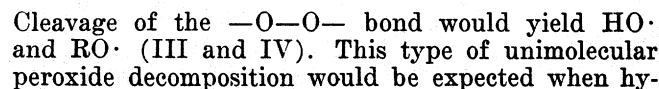
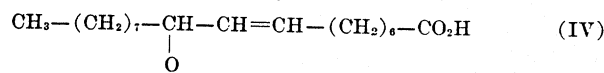
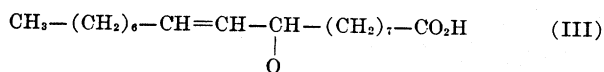


TABLE III
Yields of Products Obtained in Autoxidation of Oleic Acid in Boiling Acetic Acid (115-120°)

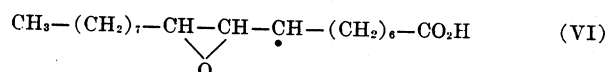
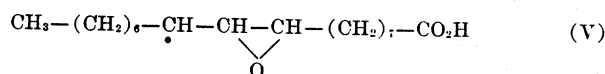
Oxidation time, hours	High-melting 9,10-dihydroxystearic acid			Cleavage products and unoxidized material			Unoxidized and hydroxy material			Polymeric residue	
	Yield %	Neut. equiv.	M.P., °C.	Yield %	Sapon. no.	Iodine no.	Yield %	Sapon. no.	Iodine no.	Yield %	Mol. Wt.
4.....	2	326	129	81	199	79	8	210	66	8	1,090
8.....	3	129	74	211	73	9	213	71	14 ^a
16.....	4	321	130	72	210	70	9	208	47	15	1,055
32.....	7	320	128	62	236	59	6	217	51	24	855
64.....	9	321	129	50	317	34	14	210	47	26	800
128.....	11	320	129	43	356	22	11	231	40	31	735

^a Insoluble.

droperoxide concentration is low (1a), as is the case when cobalt salts are present.



Both III and IV, merely by a shift of one π -electron of the double bond to couple with the odd electron on oxygen, could form the oxirane ring in the 9,10-position as shown (V and VI).



Reacquisition of a hydrogen atom by V or VI would yield the identical compound, namely, *trans*-9,10-epoxystearic acid, the product actually isolated when solvent is absent (3). In acetic acid however *trans*-9,10-epoxystearic acid is converted by ring opening to the hydroxyacetoxy compound which yields high-melting 9,10-dihydroxystearic acid on hydrolysis.

This reaction scheme also accounts for the isolation of triol, reported by earlier works for other systems (4), since the reacquisition of the HO· by V or VI followed by hydrolysis would yield a trihydroxy compound.

It should not be concluded however that high-melting, 9,10-dihydroxystearic acid is the sole dihydroxy compound formed although there is no doubt that it predominates. It has been shown by us (11), as well as by others (3, 12), that low-melting 9,10-dihydroxystearic acid is also formed. In the present investigation a 0.5-1% yield of low-melting 9,10-dihydroxystearic acid, m.p. 92° (a mixed melting point with an authentic specimen, m.p. 95°, was not depressed), was obtained from the fraction consisting of unoxidized and hydroxy material (Tables I, II, III) by saponification, acidification, and crystallization of the mixed acids successively from acetone and alcohol at 0°.

The isolation of only minor quantities of low-melting 9,10-dihydroxystearic acid strongly suggests that the formation of oxirane compounds does not occur by an epoxidation reaction between a peroxide and an olefinic compound. If epoxidation were an important reaction, appreciable quantities of *cis*-9,10-epoxystearic acid (solvent-free system) or low-melting 9,10-dihydroxystearic acid (acetic acid system) would be

isolated since oleic acid, a *cis* compound, is the predominant olefinic species present during the major portion of the autoxidation reaction, and epoxidation is known to be stereospecific. Furthermore elaidic acid cannot be present to any significant extent since we have shown (10) that the bulk, if not all, of the *trans* components formed during the autoxidation of oleic acid are *trans* peroxides and not the simple *trans* olefinic compound. Recently we have obtained more direct evidence that elaidic acid is not formed in significant quantities by demonstrating that the products isolated from the urea complexes obtained in separating unoxidized material from peroxides (in solvent-free autoxidation systems) are substantially free of *trans* materials (2).

Summary

The autoxidation of oleic acid and methyl oleate in acetic acid solution at 25-30°, 65°, and 115-120° with a cobalt salt as catalyst has been studied. Samples were withdrawn at intervals and the oxidation products were analyzed and then separated into high-melting 9,10-dihydroxystearic acid, cleavage products, unoxidized and hydroxy materials, and polymers.

The best yields of desired oxidation products were obtained at 65°. Yields of pure 9,10-dihydroxystearic acid, m.p. $\geq 128^\circ$, were 12-17% and cleavage products 64-68%, thus accounting for about 80% of the starting material. At 25-30° and 115-120°, yields of the above-mentioned products were low.

A mechanism is proposed which accounts for the formation of *trans*-9,10-epoxystearic acid from both oleic and elaidic acid autoxidized in the absence of solvent, and the consequent isolation of high-melting 9,10-dihydroxystearic acid when acetic acid is the solvent.

REFERENCES

- 1a. Bateman, L., and Hughes, H., *J. Chem. Soc.*, 1952, 4594-4601.
1. Bolam, T. R., and Sim, W. S., *J. Soc. Chem. Ind.*, 60, 50-56 (1941).
2. Coleman, J. E., unpublished results.
3. Ellis, G. W., *Biochem. J.*, 30, 753-761 (1936).
4. Farmer, E. H., and Sundralingam, A., *J. Chem. Soc.*, 1942, 121-139.
5. Gee, G., and Rideal, E. K., *J. Chem. Physics*, 5, 794-801 (1937).
6. Knight, H. B., Eddy, C. R., and Swern, D., *J. Am. Oil Chem. Soc.*, 28, 188-192 (1951).
7. Knight, H. B., Jordan, E. F. Jr., Roe, E. T., and Swern, D., *Biochemical Preparations*, 2, 100-104 (1952).
8. Knight, H. B., and Swern, D., unpublished results.
9. Ross, J., Gebhart, A. I., and Gerecht, J. F., *J. Am. Chem. Soc.*, 71, 282-286 (1949).
10. Swern, D., Coleman, J. E., Knight, H. B., Ricciuti, C., Willits, C. O., and Eddy, C. R., *J. Am. Chem. Soc.*, 75, 3135-3137 (1953).
11. Swern, D., Knight, H. B., Scanlan, J. T., and Ault, W. C., *J. Am. Chem. Soc.*, 67, 1132-1135 (1945).
12. Swift, C. E., and Dollear, F. G., *J. Am. Oil Chem. Soc.*, 25, 52-53 (1948).
13. Ueno, S., Okamura, Z., and Saida, T., *J. Soc. Chem. Ind. Japan*, 34, Suppl. binding 106-108 (1931).